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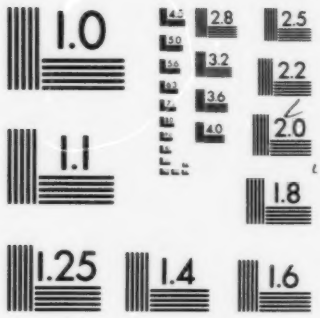

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LITERATURE SURVEY ON THE ELECTRODEPOSITION OF COPPER-ARSENIC ALLOYS

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LITERATURE SURVEY ON THE ELECTRODEPOSITION OF COPPER-ARSENIC ALLOYS

by

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ABSTRACT

The presence of arsenic in anode copper can yield better cathode purity during copper electrorefining because of increased slime adherence and can counteract anode passivation effects of other trace elements such as antimony. If insufficient arsenic is present in the metal, copper arsenides potentially may be used as doping agents during anode casting for increasing the arsenic content. Studies dealing with the characterization of copper-arsenic alloys, the electrochemistry of copper and arsenic, and copper arsenide electrodeposition as well as patent disclosures on electrolytic copper arsenide production were surveyed. Based on this literature survey, some relevant work required to determine the application of this methodology to copper electrorefining is suggested.

Keywords; arsenic, arsenides, copper, alloys, electrodeposition.

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ANALYSE DE LA DOCUMENTATION PORTANT SUR L'ÉLECTRODÉPOSITION DES ALLIAGES DE CUIVRE-ARSENIC

par

R.M. Morrison* et D.J. MacKinnon*

RÉSUMÉ

La présence d'arsenic dans le cuivre pour anodes peut permettre d'obtenir une plus grande pureté à la cathode au cours de l'électroraffinage en raison d'une adhérence accrue des colloïdes; elle peut en outre neutraliser les effets de passivation à l'anode d'autres éléments traces comme l'antimoine. Si la teneur en arsenic est insuffisante dans le métal, les arséniures de cuivre peuvent être utilisés comme agents de dopage au cours de la coulée en anodes afin d'augmenter la teneur en arsenic. Des études portant sur la caractérisation d'alliages de cuivre-arsenic, sur l'électrochimie du cuivre et de l'arsenic et sur l'électrodéposition de l'arséniure de cuivre ainsi que des présentations de brevets liés à la production d'arséniure de cuivre électrolytique ont été analysées. Compte tenu de cette analyse, il est proposé d'entreprendre certains travaux visant à déterminer dans quelle mesure cette technique peut être appliquée à l'électroraffinage du cuivre.

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INTRODUCTION

The presence of arsenic in copper complicates the aqueous acidic sulphate electrorefining process. The arsenic content of the smelted concentrate determines, in large part, the arsenic content of the cast anodes. High arsenic copper usually gives too much soluble arsenic in the tankhouse electrolyte whereas low arsenic copper results in non-adherent anode slimes during electrorefining. The former case presents an obvious problem because of arsenic buildup in the electrolyte and the possibility of arsine generation at high polarization in the liberator cells. The latter case, which is of interest here, can result in the presence of suspended or floating slimes in the electrolyte which in turn increases the impurity content of the copper cathodes.

The beneficial effect of arsenic in copper anode electrorefining arises mainly from increased slime layer stability and adherence. As a result, there are fewer suspended solids and, therefore, less chance of their inclusion as impurities in the cathode. Most of the soluble arsenic encountered in copper refineries is As(V) (1). It appears that there is a minimum level of arsenic in the anodes which is desirable.

Arsenic and antimony, when present together in the anode, exhibit synergistic effects towards anode passivation and copper cathode purity. It has been reported that 400 ppm As contained in a copper anode will counteract the effect of 250 ppm Sb. A solution As:Sb ratio of 2:1 gives the minimum amount of arsenic which is beneficial (2). At lower arsenic contents, this 250 ppm Sb-containing anode would quickly passivate.

In processing copper derived from high-antimony copper ores, it may be beneficial to add additional arsenic prior to anode casting.

A possible means of increasing the arsenic content of anode copper when insufficient arsenic is present in the concentrate is to dope the copper melt with arsenic prior to anode casting. Since arsenic trioxide, the most readily available form of arsenic, is volatile, alloys probably will have to be used for doping purposes. The presently available copper arsenides are quite pure and expensive since they are prepared by thermal synthesis from the constituent elements. It may be possible to use a copper arsenide mixture, obtained as an electrodeposit from copper electrolyte containing added arsenic, as the doping material. In practice, the addition of arsenic (III) to the copper refinery's secondary liberator cell electrolyte may result in the production of copper arsenides at the cathode that are suitable for doping the cast anodes with arsenic.

It should be noted that other sources of crude copper arsenides are available. Speiss from lead smelting can contain 55 to 69% Cu and 15 to 20% As along with lead (6 to 14%) and antimony (1.0 to 11%) (3). The cathode sludge from the exhaustive electrolysis of copper liberator electrolyte contains mainly copper arsenides along with other elements (4,5). These sources give crude products which may create further problems during anode casting and electrorefining. Also, these sources may not be available to all copper smelters.

The copper-arsenic phase system has been well researched. Electrochemical studies of copper-arsenic deposition from copper electrolyte have

been reported. Also, a patent on copper-arsenic removal from copper electrorefining electrolyte based on copper arsenide production has been described. The purpose of this report is to bring together the information which now exists on these various subjects and to make a critical evaluation of the application of this technique for typical secondary liberator cell electrolytes.

COPPER-ARSENIC ALLOYS

The copper-arsenic phase diagram of Naud and Priest (6) is illustrated in Figure 1 and some properties of the copper arsenides are listed in Table 1. Most of the compounds have been synthesized by high temperature solid state diffusion although crystalline Cu_2As was formed by wet (solution) oxidation of higher copper content phases. Figure 1 does not reflect all the complexities of the system, however. The α phase of copper can contain up to 7% As in solid solution. Between 11 and 23% As, the ε phase of nominal stoichiometry Cu_6As (algodonite) is found, but the composition ranges from Cu_4As to Cu_9As. The next phase is $Cu_{15}As_4$ at 24% As; previously this was thought to be α-$Cu_{3-x}As$. The arsenic alloys, β-$Cu_{3-x}As$ and $Cu_{5-x}As_2$, exist at 28 and 32% arsenic, respectively ($x=0$); they can be copper deficient ($x\neq0$) and contain higher arsenic. The highest arsenic containing compound shown is Cu_2As which is 37% arsenic.

As noted in Table 1, these alloys have different structures and thus, can be differentiated by X-ray diffraction (XRD) analysis. The α phase of copper has a cubic close packed structure and the ε (algodonite) phase displays hexagonal symmetry with the space group $P6_3/mmc$ and

Z=2 (7). The 24% As phase belongs to a cubic group and is thought to be isostructural with $Cu_{15}Si_4$ (7). The β-$Cu_{3-x}As$ compound shows trigonal symmetry (6, 8, 9) with the space group $P\bar{3}c1$ (Z=6) and an anti-LaP_3 structure; some mention is made of a hexagonal modification in the mineralization of β-domeykite (8, 9). $Cu_{5-x}As_2$ possesses a Ga_2Mg_5 type structure with the space group orthorhombic Ibam (Z=4, (10)). Cu_2As has a tetragonal Cu_2Sb type structure with the space group P4/nmm and Z=2 (6).

Oxidative leaching of Cu_2As (11) gave an amorphous residue but the leach solution analysis indicated that $Cu_{1.5}As$ and CuAs may have been formed by selective removal of Cu. Thus, there is some evidence that the copper arsenides (Cu_2As, $Cu_{1.5}As$ and CuAs) may have some features of the copper sulphides (chalcocite, digenite and covellite) where copper deficient compounds form. Unfortunately, these are not well identified for the arsenides.

It is interesting to note that Cu_3As is formed at low copper concentrations at copper surfaces during the hydrogen reduction of spent copper electrolyte (12). The reaction, however, is very slow. Both $Cu_{3-x}As$ and $Cu_{5-x}As_2$ have been synthesized by the action of arsine on cupric ion solutions (13). Also, copper arsenide formation was observed during copper cementation of soluble arsenic from chloride solutions (14). The formation of copper arsenides by the addition of copper salts or arsenic(III) solutions during the flotation of chalcopyrite and arsenopyrite (15) and nickel arsenide (16) is thought to aid in their separation from non-copper or non-arsenide minerals, mainly pyrite.

Substitution of other base metals for copper in copper arsenides

is not common. This is unlike the Fe-Co-Ni arsenides (17, 18) where series of isomorphous compounds of variable metal content are formed. There has been one report of silver-rich domeykite ($Cu_{3-x}As$) (19) where 50% Ag substitution for copper was reported. It is, perhaps, not surprising that the heavier Group Ib metals will substitute with copper arsenides because of the low formal oxidation state (+1) of the copper in these compounds. Iron, Co and Ni generally occur in higher oxidation state compounds whereas the Ib metals usually exist in lower oxidation state compounds. Recently, a series of ternary arsenides with Group Ia and IIa (i.e., non-transition) metals has been reported (20-23).

Some other properties of the arsenides have been explored. The conductivity and magnetic susceptibility of $Cu_{3-x}As$, $Cu_{5-x}As_2$ and Cu_2As have been reported (24); the ε phase is always obtained as a mixture with the α phase and $Cu_{3-x}As$. It was not pure enough for these measurements. In addition, data on the oxidation and hardness of some arsenides are tabulated (25).

ARSENIC ELECTROCHEMISTRY

The reduction half-cell reactions for soluble As(III) and As(V) to elemental arsenic are (26):

$$H_3AsO_3(aq) + H^+ + 3e^- = As + 2H_2O \qquad E^o = 0.25\ V$$

$$H_3AsO_4(aq) + 5H^+ + 5e^- = As + 4H_2O \qquad E^o = 0.65\ V$$

The electrochemical reduction of As(V) to As(III) can be kinetically slow. A further reduction of arsenic to arsine gas is described by:

$$As + 3H^+ + 3e^- = AsH_3(g) \qquad E^o = -0.698\ V$$

Arsine is extremely poisonous and 10^{-3} atmospheres is lethal to man. More

recent work has given a reversible reduction potential of -0.220 V for the arsenide reaction (27). The more positive value (-0.220 V) for the standard reduction potential is more likely to be correct since the other value may contain overpotential (nucleation, etc.) terms. The arsine evolution reaction may be more favorable than previously thought. An E_h-pH diagram is depicted in Figure 2 where the AsH_3 stability field is given at pressures of 1 atm and 15 ppb. Copper electrorefining electrolyte can generate arsine at high polarization when most of the more noble elements have been reduced; for instance, at 226 Am^{-2}, an electrolyte containing 5-6 gL^{-1} arsenic (mainly as As(V)) gave arsine if less than 3 gL^{-1} Cu were present (28).

Studies (29) on the electrodeposition of As(III) from acidic sulphate and chloride solutions have shown that elemental arsenic deposits only at high overpotentials; i.e., not at the reversible potential. Even then, poor current efficiencies (< 50%) are exhibited that decrease with time (30). This last characteristic is attributed to the non-metallic nature of the deposited amorphous arsenic. Arsenic in the elemental state is a "semi-metal" which has poor metallic properties such as conductivity and lustre.

An E_h-pH diagram (31, 32) formulated for a copper-arsenic solution containing 0.6 mol dm^{-3} Cu^{2+}, 0.01 mol dm^{-3} As(III) over the pH range -2 to +2 is depicted in Figure 3. The $Cu_{2.4}As$ phase shown in the figure corresponds to the $Cu_{5-x}As_2$ phase. The formation of copper arsenides under mildly reducing conditions without the formation of elemental arsenic is predicted.

The electrochemistry of copper arsenide electrodes also has been studied. During electrochemical oxidation studies, Bombach et al. (31) found

that arseniferous copper containing 3% As dissolves leaving a firmly adhering slime of β-$Cu_{3-x}As$ at 50 Am^{-2} and $Cu_{5-x}As_2$ and β-$Cu_{3-x}As$ at 300 Am^{-2}. The copper arsenide electrodes $Cu_{5-x}As_2$ ($Cu_{2.4}As$), β-$Cu_{3-x}As$ and Cu_6As have been shown to generate arsine at lower potentials (33) than noble electrode materials.

The presence of Cu(II) in solution is known to interfere with the polarographic determination of trace As(III) concentrations. It is proposed that copper arsenide rather than elemental arsenic is the reduction product at the mercury cathode; the reduction current is proportional to the copper concentration and not the arsenic concentration. The nature of the mercury surface is altered owing to the solubility of copper arsenides in mercury; reduction currents due to arsine or hydrogen gas evolution are seen at less negative potentials than predicted in these copper(II)-arsenic solutions (34). Analytical methods for arsenic based on cathodic stripping voltammetry (34) and anodic stripping voltammetry (glassy carbon electrodes) (35) of copper arsenides have been reported.

ELECTRODEPOSITION OF COPPER-ARSENIC ALLOYS

Dewalens et al. (33) have studied many aspects of the electrodeposition of Cu-As alloys. They found that arsenic does not deposit near its reversible potential on platinum in 500 gL^{-1} H_2SO_4 medium. For an electrolyte containing copper sulphate and arsenite (20 $gL^{-1}Cu^{2+}$, 5 gL^{-1} As(III), the voltammogram scanned negatively from + 0.400 V (NHE) showed a cathodic current at + 0.33 V which levelled off at 20 mA cm^{-2} at more negative potentials. This current was assigned to copper reduction since

copper in acidic sulphate solution is more noble than the arsenides and will deposit first:

$$Cu^{2+} + 2e^{-} = Cu(s) \qquad E^{o} = + 0.337\ V$$

At potentials cathodic to + 0.200 volts, there is a reduction current superimposed on the copper reduction current that levelled off at 30 mA cm^{-2}. Although arsenic will not deposit in the absence of copper at this potential, it will deposit in this cupric solution. There was, however, no evidence for the deposition of elemental arsenic. If the molar ratio of Cu/As is greater than 2.25, there are only two peaks in the voltammogram that are due to first copper and then copper arsenide reduction. At Cu/As ratios lower than 2.25, there were three peaks observed, the most cathodic of which was attributed to arsine generation. The authors found As(V) to be inactive to deposition under these conditions and this point may be significant as As(V) is the dominant species in copper electrolytes.

Other important data are:

1. The solubility of arsenic(III) is 4 gL^{-1} at 25°C, 7.5 gL^{-1} at 50°C, and although not exactly determined > 10 gL^{-1} at 90°C (supersaturated solutions are formed and the apparent solubility may decrease with time in all cases).

2. The conditions studied were: 5 gL^{-1} As(III), 5 and 20 gL^{-1} Cu(II) (high relative arsenic and high relative copper, respectively). Most work was done at 50°C and 500 gL^{-1} H_2SO_4 (5 M).

3. The voltammetry curves are dependent on temperature. For example, the limiting current density at 50°C for the second peak is 10 mA cm^{-2} whereas it is 15, 5 and 2 mA cm^{-2} at 75, 25 and 0°C, respectively.

4. There did not appear to be a sharp boundary between the formation conditions for the different Cu-As phases.

The alloys formed at the limiting current of the second wave for high relative arsenic concentrations were $Cu_{5-x}As_2$ in mixtures with some Cu_2As, β-$Cu_{3-x}As$ or (sic) α-$Cu_{3-x}As$ (most likely $Cu_{15}As_4$). At less than the limiting current of the second wave at high relative arsenic concentrations, β-$Cu_{3-x}As$ was obtained. At high relative copper concentrations, the copper rich phases, β-$Cu_{3-x}As$, (sic) α-$Cu_{3-x}As$, ε phase, and α copper were identified by XRD. It is obvious that the proportions of copper and arsenic at the surface rather than the magnitude of the deposition potential define the alloy composition and copper arsenide alloy deposition. This is a case of maximal induction alloy deposition according to Brenner's classification (36).

Dewalens et al. (33) stated that the composition of the alloys can be estimated from the partial currents of copper deposition and copper-arsenic alloy deposition. Given the voltammogram (ref. (30)) of 5 gL^{-1} As(III), 20 gL^{-1} Cu(II), and 500 gL^{-1} H_2SO_4 on a copper electrode at 50°C, it can be estimated that the copper and alloy deposition reactions proceed at 20 and 10 mA cm^{-2}, respectively. Table 2 shows the calculated arsenic contents for codeposited copper and copper arsenide for each identified copper arsenide. The arsenic content varies from 2.3% for α copper to 12.4% for the most arsenic rich phase. For low relative copper electrolytes, the partial currents of codeposition also were estimated (30) and the corresponding calculated arsenic contents also are presented in Table 2. Although the high copper electrolytes give high copper products and the relatively low copper electrolytes give relatively low copper products, the actual arsenic contents of the deposits were not determined because the authors found it impossible to measure arsenic concentrations, in the presence of copper, by atomic absorption spectrophotometry with their instrumentation. More modern instrumentation

has now surmounted this problem and the measurement of arsenic in copper containing solutions is a fairly simple and accurate analysis (34).

Although the low copper electrolytes give higher arsenic content products, the rates of arsenic deposition are lower as can be determined from the voltammetry curves of ref. (33). The rate of arsenic deposition was calculated assuming a 10% arsenic product, and the data are listed in Table 3. Also, relatively low copper concentrations appear to give a heightened possibility of arsine gas production. Controlled potential (potentiostatic) deposition may be necessary to prevent the arsine reaction. Most electrolytic operations employ constant current (galvanostatic) deposition although potentiostatic methods have been found necessary (38) to maintain product quality and acceptable current efficiencies for some alloy systems.

Soviet workers (39) reported that in the electrolytic reduction of an ammoniacal leach solution from the autoclave processing of a complex ore, a small amount of base metal arsenide similar to skutterudite ($NiAs_3$) and of stoichiometry $(Co_{0.8}Ni_{0.2})As_3$ was formed. This is the only report found that described the electrochemical production of a base metal arsenide other than copper. This report is only partially relevant because of the basic electrolyte (acidic solutions were used in the copper arsenide work), the high proportion of arsenic in the product (low arsenic levels are expected in copper arsenides), and the low yield of the arsenide obtained. Brenner (36), however, does make reference to a 1939 paper wherein nickel arsenides were electrodeposited from a boric acid nickel plating bath.

Selenium (40) and antimony (33) have been reported to electrodeposit

as alloys with copper. These elements should not be a concern for copper arsenide production as copper is less noble than either of them, and they should be cemented out by copper before their concentrations become too great.

COPPER ELECTRODEPOSITION PATENT

Japanese workers have patented a process for removing copper and arsenic from copper electrolyte (41). The decoppered electrolyte from a copper sulphate plant (42) associated with a copper electrorefining operation was electrolyzed to give copper-arsenic products. A copper sulphate plant is one alternative for controlling copper and impurity buildup. North American electrorefiners, however, generally do not favor a full scale copper sulphate plant because of the large capital costs involved (40) and the limited market for copper sulphate. The soluble arsenic existed mainly in the +5 state and had to be converted to the +3 state before the electrolysis was successful. The method of arsenic(V) reduction was not specified but chemical reactions were recommended. The patent disclosure indicated that during the electrolysis of As(V)-containing solutions, the copper concentration decreased from $> 13\ gL^{-1}$ to $< 1\ gL^{-1}$ whereas the arsenic concentration decreased from 12.5 gL^{-1} to 6 gL^{-1}. Continued electrolysis resulted in cathode polarization and arsine gas generation.

Table 4 shows the composition of the electrodeposits for the various copper-arsenic concentrations in solution. The conditions of electrolysis were:

cathode: copper plate

anode : lead plate

cathode potential: -200 mV

electrolysis time: 2 h

stirring: nitrogen gas sparging

The constant potential electrolyses gave mainly Cu_2As and $Cu_{3-x}As$ for the As(III) solutions and mainly Cu metal and some Cu_2As for the As(V) solutions. It should be noted that the deposits from the As(III) electrolyses were only about 86% (Cu + As) whereas most of the deposits from the As(V) electrolyses were > 95% (Cu + As). The authors did not state the balance of the deposit although the electrolyte contained 15 gL^{-1} Ni^{2+}; it is unknown whether this is due to additional arsenide reduction or poor analytical technique. The relative amount of arsenic contained in the deposit was less for the As(V) experiments than for the As(III) tests, and this is consistent with the relatively inert behaviour of As(V) towards electrochemical reduction. The deposit Cu:As molar ratios are close to 2:1 for the As(III) experiments and > 10:1 for the As(V) tests.

Unfortunately, the patent disclosure does not provide current efficiencies or the extent of arsenic depletion obtained in the electrolysis bath.

The data given in the Japanese patent correlate well with the electrochemical work of Dewalens et al. That the Japanese workers found relatively high arsenic deposits from the solutions containing relatively high arsenic concentrations would be predicted by the electrochemistry. The use of potentiostatic electrolysis or periodic current reversal (25) to avoid cathodic polarization and arsine gas generation would be prudent for the dilute copper solutions.

ELECTROREFINERY ELECTRODES

The composition of a typical feed to the primary liberator cells is given in Table 5. The stripper (liberator) section, uses insoluble lead alloy anodes and copper starter sheets; commercial grade cathodes are obtained from this process. The purpose of the liberator cells is to remove excess copper generated in the tankhouse and to help control impurity buildup. In most electrorefineries there are two sets of liberator cells. In the primary liberators, the copper concentration is reduced from 44 to 25 gL^{-1} but a portion of the electrolyte then is sent to the secondary liberator cells where the copper concentration is reduced to 8 gL^{-1} or lower. The spent electrolyte from these cells is used for slimes leaching. It is proposed to use the electrolyte from the secondary liberator cells for copper arsenide alloy deposition. The solution characteristics most likely are:

Cu^{2+} : 8 gL^{-1}

H_2SO_4 : 190 gL^{-1}

As : 1.5 to 5.0 gL^{-1}

Ion chromatographic examination of typical electrorefinery solution has shown that the majority of the arsenic is in the +5 oxidation state (1). As(III) is necessary for successful electrowinning of copper arsenide. It is difficult to ascertain whether it is cheaper or easier to add As_2O_3 rather than attempt to reduce the As(V) chemically. The other impurities would be expected to be similar to those values listed in Table 5, since copper is electrowon and acid is produced in the liberator cells.

OUTLINE OF SUGGESTED WORK

Obviously, compounds containing arsenic and copper will be produced

under reasonable electrolysis conditions. It is certainly known that As(V) will not be electroactive and that the solution (Cu(II), As(III)) compositions will determine the alloy composition. The current efficiencies, the deposition rates, or the exact correspondence of the copper/arsenic solution concentrations to the copper/arsenic alloy content over a wide range of concentrations are not known. The question of arsine generation is an important one. Is the electrodeposition to be restricted to high copper electrolytes and/or potentiostatic electrolysis? Periodic current reversal (25) or galvanostatic electrolysis where the current density is lowered with time are other techniques which might be employed. Arsine gas evolution is an important consideration since galvanostatic electrolysis is much more practical.

Specifically, the conditions of electrolysis to be explored are relatively high copper concentrations (20 gL^{-1}), low relative As(III) concentrations (5 gL^{-1}) and acid concentrations of 100 to 500 gL^{-1} H_2SO_4 at a temperature of 50°C The danger of gas evolution will be minimized under such conditions although it is still a concern. The polarization curves generated using this electrolyte will determine the electrolysis conditions; the previous work suggests that 30 mA cm^{-2} or -100 mV NHE will be the cathodic current and potential limits, respectively. Deposits obtained from the experiments will be analyzed for metal contents and the corresponding current efficiencies will be calculated. As well, the effect of impurities such as high nickel concentrations and soluble iron and cobalt on the deposits should be ascertained. The concentrations of copper and arsenic employed should resemble the plant solutions as closely as possible.

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Table 1. Some properties of the common copper-arsenic alloys

Compound or phase	%As (% atomic)	Description
α phase Cu	up to 7%	arsenic in solid solution (cubic structure)
ε phase "Cu_6As"	12% to 23% 16%	"algodonite" variable composition between Cu_9As (12%) and Cu_4As (23%) (hexagonal structure)
$Cu_{15}As_4$	24%	α-domeykite originally formulated as α-$Cu_{3-x}As$ (cubic structure)
β-$Cu_{3-x}As$	28% (x=0)	β-domeykite (trigonal structure) x=0.4 to 0.15 at 300° in synthetic samples
$Cu_{5-x}As_2$	33% (x=0)	x=0.1, low temperature orthorhombic structure
Cu_2As	37%	isostructural with Fe_2As, non-metallic appearance, violet in colour (tetragonal structure)

Table 2. Calculated arsenic contents of the electrodeposits based on partial currents

Arsenide	% As in product				
	Cu(II) = 20 gL^{-1} As(III) = 5 gL^{-1}	Cu(II) = 5 gL^{-1} As(III) = 5 gL^{-1}			
	T=50°C	T=0°	T=25°	T=50°	T=75°
α-phase Cu (7% As)	2.3	3.5	3.1	3.3	4.1
ε phase Cu (16.4% As)	5.5	8.2	7.2	7.7	9.5
$Cu_{15}As_4$ (23.9% As)	8.0	12.0	10.5	11.2	13.9
β-$Cu_{3-x}As$ (28.2%)	9.4	14.1	12.4	13.3	16.4
$Cu_{5-x}As_2$ (32.0%)	10.7	16.0	14.1	15.0	18.6
Cu_2As (37.1%)	12.4	18.6	16.3	17.4	21.5

Table 3. Rate of arsenic deposition at an electrode and assuming a 10% As-90% Cu phase

Cu(II)* (gL^{-1})	T (^{o}C)	Rate of arsenic deposition $gL^{-1}cm^{-2}$
20	50	2.8×10^{-3}
5	0	1.9×10^{-4}
5	25	4.2×10^{-4}
5	50	8.8×10^{-4}
5	75	1.4×10^{-3}

*As(III) = 5 gL^{-1}
H_2SO_4 = 500 gL^{-1}

Table 4. Composition of electrodeposits from copper-arsenic electrolyte*

(i) As as As(III)

Cu gL^{-1}	As gL^{-1}	% in deposit Cu	% in deposit As	Cu + As total	Cu : As molar ratio
1	1	48	33	84	1.71
1	3	50	30	80	1.96
1	8	50	30	80	1.96
3	3	43	33	76	1.54
6	5	54	30	84	2.13
10	8	52	29	83	2.11

(ii) As as As(V)

1	1	89	11	100	9.5
1	3	88	10	98	10.4
1	8	88	9	97	11.5
3	1	91	6.6	98	16.3
3	3	86	10	96	10.1
6	3	89	7	96	15.0
6	5	85	9.2	94.2	10.9
6	8	88	9.7	97.7	16.7
10	5	89	4.6	93.6	22.8
10	8	91	6.2	97.2	17.3

* electrolyte contains 15 gL^{-1} Ni^{2+}, 400 gL^{-1} H_2SO_4

Table 5. Composition of typical electrolyte to primary liberator cells (44).

Element	Concentration (gL^{-1}) Kidd Creek	CCR	Inco Copper Cliff
Cu	46	42.2	40 - 45
H_2SO_4	150	150	160 - 175
As	1.5	5	1.6
Sb	0.1	0.45	0.05
Bi	0.07	0.09	0.1
Ni	8.0	17.1	20 - 25
Cl	0.020	0.031	0.24

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Figure 1 Phase diagram for the copper-arsenic system.

Figure 2 E_h-pH diagram for the arsenic-water system.

Figure 3 E_h-pH diagram for the copper-arsenic-water system (Cu(II): 0.6 mol dm^{-3}; As(III): 0.01 mol dm^{-3}).

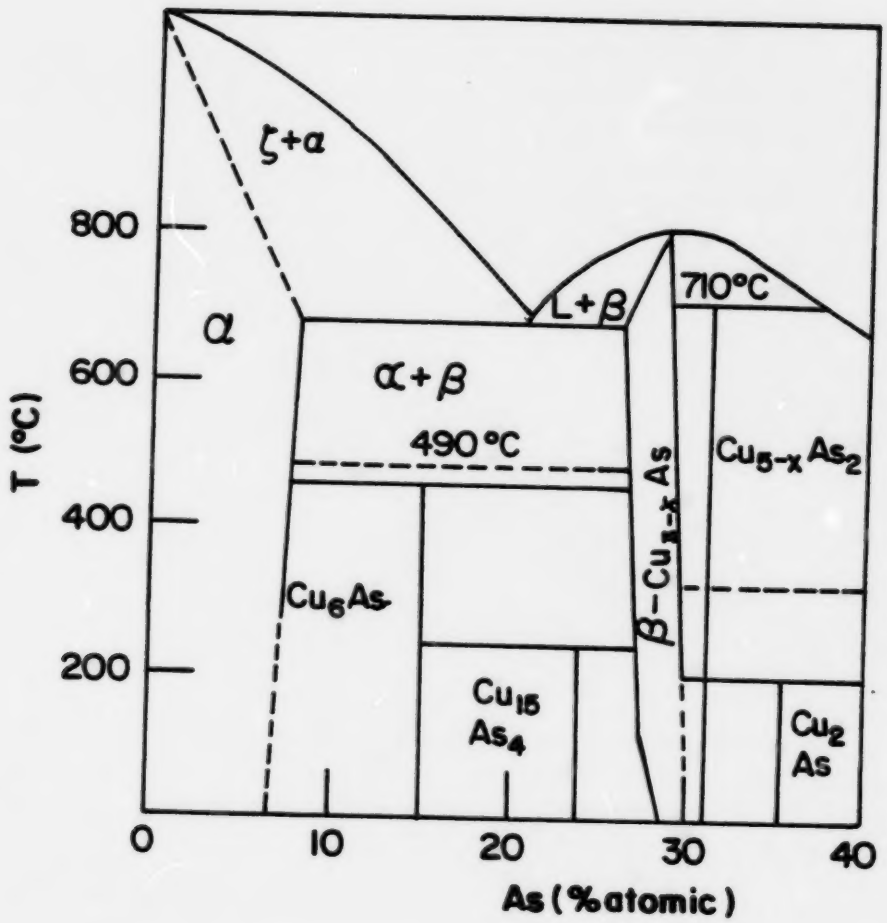

Fig. 1 - Phase diagram for the copper-arsenic system.

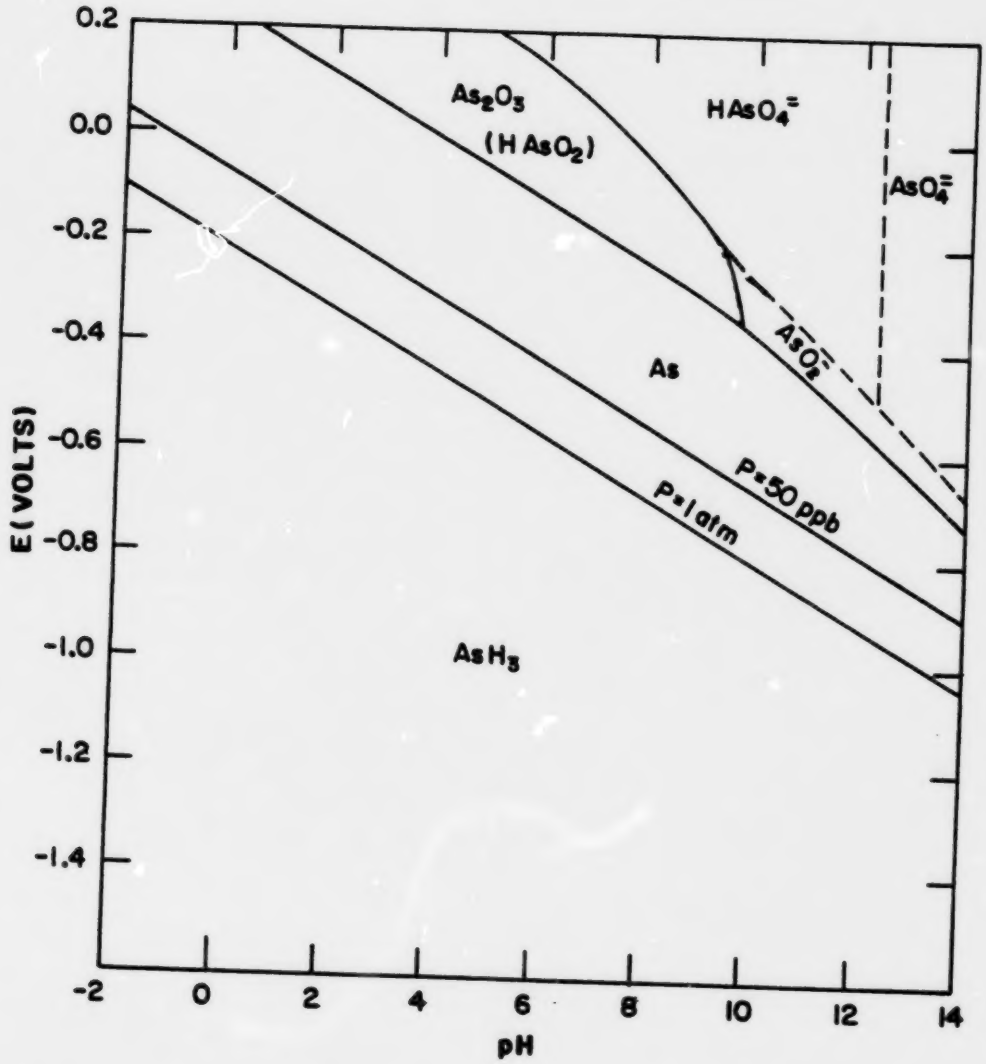

Fig. 2 - E_h-pH diagram for the arsenic-water system (unit activities for all species except arsine).

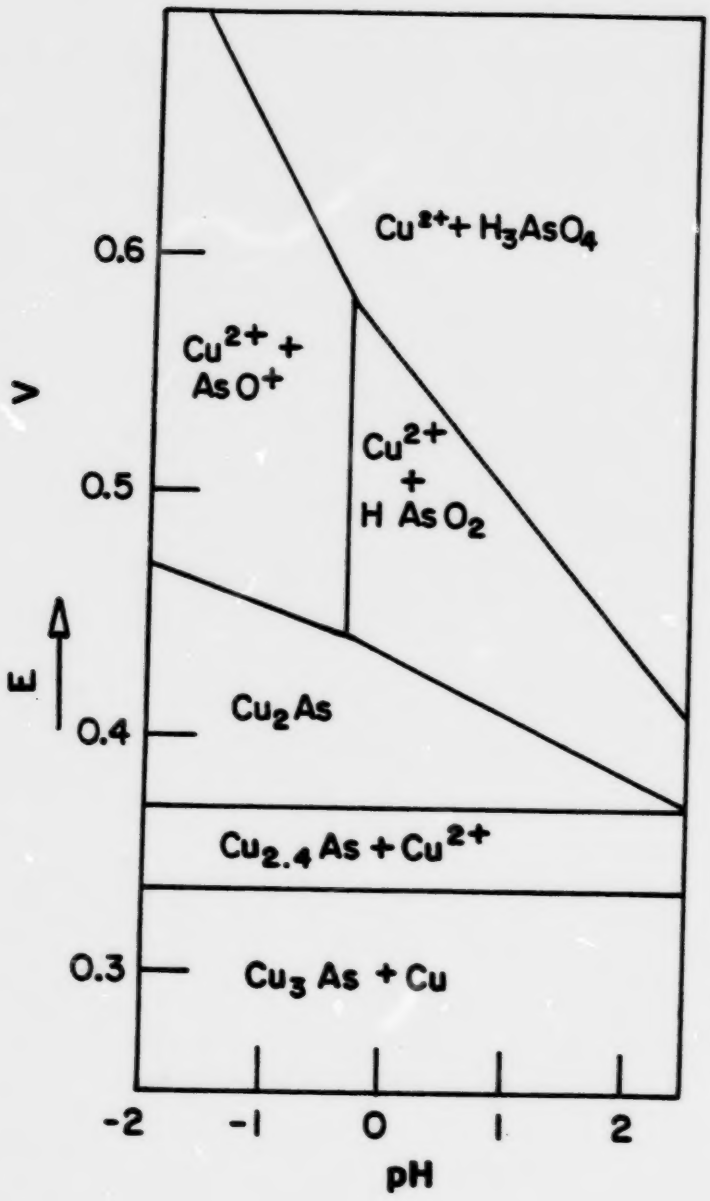

Fig. 3 - E_h-pH diagram for the copper-arsenic-water system (Cu(II): 0.6 mol dm^{-3}; As(III): 0.01 mol dm^{-3}).